TRENCH PROCESS AND APPARATUS FOR DYE REMOVAL FROM DENIM SCRAP

Inventors

Gary F. Hirsch, Robert T. Patton and David M. Hall

BACKGROUND

Field of the Invention

This invention relates to an apparatus and process for removing indigo dye from denim scrap. In particular, the process of this invention is directed to a method for removing indigo dyes from scrap textiles such as denim scrap where the vat dyes have been applied in a reduced, soluble "leuco" form and oxidized to precipitate the dye in and on the fabric in an insoluble, or oxidized, form.

Background of Related Art

Cotton and other cellulose scraps produced when cutting cotton fabrics in clothing manufacture are a waste product typically buried in landfills or consumed in incinerators. Garnetting to separate and recover the cotton fiber shortens the fiber length and the products had few uses. As a consequence, over 200 million pounds of denim scrap in the U.S.A. alone, is destroyed as waste each year.

U.S. Patents 5,376,143 and 5,471,720 describe a process for recycling denim waste by separating the fibers, preparing a colored yarn of a blend of the recycled fibers and virgin fibers, and preparing denim or similarly dyed fabric from the yarn. This process has not been commercially implemented, perhaps because of costs of fiber separation and the limitations of the shortened fibers in the making a strong, durable fabric.

Many applications of cotton, however, do not require long fibers. Cotton batting is a popular absorbent because of its softness and cushioning characteristics and high water absorbency. It is a preferred component for many industrial, household and particular medical products such as quilts, upholstery, sanitary napkins, diapers and medical products such as swabs, bandages and the like. However, most of these applications require the cotton fibers be colorless and strong, and a process for

recycling cotton scrap to produce cotton fibers for these applications has not been commercially feasible because of the difficulties in processing the scrap. One principal area of difficulty is removal and/or decolorizing the vat dyes present in many cotton scraps such as denim.

Vat dyes consist of colored compounds that are usefully precipitated on and within cellulosic fibers. These compounds are reversibly changed to a water-soluble "leuco" state by chemically reducing them. This is done easily by mixing the dye into a water solution containing a water- soluble reducing agent such as sodium hydrosulfite along with alkali such as caustic soda. In a dying process, the cellulose fiber is typically immersed in such a reduced, leuco solution, and the dye is allowed to penetrate the substrate. After this immersion, the fiber is exposed to an oxidizing environment. Such an environment is air and in one such process, the yarn, wetted in a leuco solution is draped in long beams over rolls and exposed to air until the dye and accompanying reducing agents are oxidized. Dilute hydrogen peroxide is also used for this oxidation. In each case, the oxidized medium converts the leuco dye to a water-insoluble state. If the dye molecule is contained within the cellulose substrate, the water-insoluble dye is trapped and cannot be removed by casual exposure to water and detergents.

Fabric is often dyed with more than one form of leuco dye. It is a common practice to dye dark shades of indigo first with the leuco form of black sulfur dye and second with the leuco form of blue indigo dye. Both dyes require subsequent oxidation to render them water-insoluble.

U.S. Patent 5,366,510 describes a process for desizing and color fading indigo dyed garments by contacting them with a reducing agent in an aqueous solution to extract dye materials before the fabrics are bleached to produce the faded, "stone washed" or "acid washed" appearance popular with denim materials. The dye is removed in a conventional rotary drum washer-extractor. Treatment of denim scrap by this procedure tends to produce tightly rolled up scrap pieces from which all of the dye is not extracted or to unravel the scraps, producing useless balls and tangles of yarn and fabric scraps or individual yarn pieces which foul the washer extractor.

For the economical recovery of useful products from textile scraps such as denim scraps, dye removal and recovery is highly desirable. The value of the recovered dye partially offsets the costs of the recycling. Also, the recovery removes an undesirable component from the waste water.

Solvent removal of dyes from synthetic fabrics is a known procedure. U.S. Patent 1,839,819 describes a method for removing dyes from synthetic textiles using heated organic solvents selected to swell the cellulose acetate and cellulose ether fibers and remove solvent soluble dyes without any

chemical change of the dyes, thus preserving them for reuse.

However, an effective solvent extraction system for textile scraps like denim scraps has not been feasible. The solvent removes size, softeners, surfactants, finishes and fully oxidized dye from the fabric, producing a solution of these components. Solvent evaporation yields a cake or solution of these components which is useless without a further, expensive purification process.

In U. S. patent no. 5,989,296 a process is described for removing indigo dye from denim scrap by extracting the fabric with an organic solvent in which the indigo dye is soluble at elevated temperatures. In this process, the solvent is cooled and extracted with an aqueous phase containing a reducing agent, and the aqueous phase is treated to oxidize and recover the indigo dye or, alternatively, the dye is recovered from the solvent by concentration and precipitation.

U.S. Patent 5,366,510 describes a process for desizing and color fading indigo dyed garments by contacting them with a reducing agent in an aqueous solution to extract dye materials before the fabrics are bleached to produce the faded, "stone washed" or "acid washed" appearance popular with denim materials. The dye is removed in a conventional rotary drum washer-extractor. Treatment of small denim scrap in this procedure tends to unravel the scraps, producing useless balls and tangles of yarn and fabric scraps which foul the washer extractor.

SUMMARY

One object of this invention is a highly effective process for treating denim scrap with extraction solvents for extracting the majority of dye from denim to yield a scrap lightly tinted with indigo dye residue.

A further object of this invention is a highly effective process for treating denim scrap with a reducing solution to remove dye from the fabric.

Another object of this invention is a highly effective process for treating denim scrap with a catalyzed hydrogen peroxide bleaching process to remove the remaining color in the fabric.

Another object of this invention is the use of a novel, inexpensive trench apparatus for use in the above processes.

Another object of this invention is a process for the countercurrent extraction of dye from fabric scrap, the purpose of which is to produce extraction liquor effluent containing the highest possible concentration of dye to facilitate the easiest subsequent dye recovery step utilizing the most compact and least expensive equipment.

Another object of this invention is a process consisting of a plurality of separated treatment vats, each equipped with a recirculation pump capable of moving the optimum flow of extraction liquor through the bags in the vat/trench. This is necessary since the desired ratio of overall liquor production to overall fabric treatment rate would not otherwise produce the desired face velocity of liquor through the fabric bed, i.e. gallons per minute of liquor per square foot of trench cross sectional area. This recirculation is accomplished by means of a pump or pumps taking suction at the bottom of the upstream end of an individual treatment vat and discharging the liquor at the bottom of the downstream end of said individual treatment vat.

A still further object of this invention is a process which raises the individual bags of liquor saturated fabric above the level of the liquor in the trench and allows the liquor to drain from the bag in a direction perpendicular to the normal flow of liquor in the bag.
This has the desirable effect of causing flow of liquor perpendicular to the mean orientation of parallel pieces of scrap fabric.

In summary, the trench apparatus for liquid treatment of fabric of this invention comprises a longitudinal trench for holding a treatment liquid. A pull rope, chain, or cable having a plurality of

shackle rings or shackles attached thereto for securing one or more bags to the rope, chain, or cable is positioned for pulling one or more bags containing dyed fabric in a longitudinal direction down the length of the trench. The pull rope, chain, or cable engages a pulley, sheave, or sprocket. An untreated fabric platform is adjacent one end of the trench, and a treated fabric platform is adjacent the other end of the trench. The trench has a liquid treatment zone with a surface level, and the trench includes one or more raised platforms dividing the trench into a plurality of separated treatment vats, the raised platforms having a height extending above said surface level. A conduit communicates from at least one vat to at least one other vat at a level below said surface level for movement of liquid therebetween. Furthermore, the separation of the trench into separate vats by means of the raised platforms allows the recirculation of the liquor contained within each individual vat at a rate which facilitates the optimum extraction rate of dye from the scrap fabric. Additionally, the raised platforms cause the gentle movement of fabric pieces as the bags are pulled over said platforms. This facilitates the optimum exposure of all surfaces of individual scrap pieces so as to eliminate the possibility of any such surface going through the entire extraction process without seeing an adequate quantity of extraction liquor. Furthermore, the process of raising each liquor saturated bag above the liquid level of the liquor in the trench facilitates draining of that liquor contained within the bag in a direction perpendicular to the normal flow of liquor through the bag. This process insures an additional degree of extraction uniformity by providing still more opportunity for the liquor to flow through the pieces of fabric. The entire portion of the trench devoted to the extraction of dye by means of a reducing agent may be advantageously covered with an airtight cover which retains an inert gas or an oxygen depleted atmosphere. This has the effect of eliminating the useless reaction of oxygen with either the leuco form of the dye or with the reducing agent itself.

The trench apparatus can be used to treat one or more of said bags containing fabric, and the trench has a liquid treatment zone, the bags being dimensioned when full to block liquid flow down the trench.

In a preferred embodiment, one or more of said bags contain denim scrap. The denim scraps within the bags will lie essentially parallel to each other in such a manner that the scrap pieces are prevented from coiling, balling or becoming distorted during the treatments.

The treatment liquid can be a dye solvent, aqueous reducing solution of aqueous bleach, or dyes, chemicals or reagents that may assist in enabling optimization of the fabrics of this invention for utilization in subsequent processes or end use applications, for example. In a preferred embodiment, the

dyed fabric is denim, and the treatment solution is a solvent for water-insoluble indigo. In another preferred embodiment, the dyed fabric is denim, and the treatment solution is an aqueous solution containing a reducing agent for indigo.

In a still further embodiment, the dyed fabric is denim, and the treatment solution is an aqueous bleach for reducing color of indigo. The aqueous bleach can be a hydrogen peroxide bleach which may contain a bleaching catalyst which is optimally a water-soluble quaternary amine catalyst.

In summary, the process of this invention for treating fabric with a liquid comprises the steps of (a) moving a bag containing said fabric down a first longitudinal vat containing liquid at a level wherein longitudinal movement of liquid in the vat is blocked by the bag, whereby longitudinal movement of the bag causes liquid to flow through the bag in a direction counter to the movement of the bag; (b) moving the bag from the vat across a drainage platform to allow excess liquid to flow from the bag; (c) moving said bag containing said fabric down a second longitudinal vat containing liquid at a level wherein longitudinal movement of the bag causes liquid to flow through the bag in a direction counter to the movement of the bag; and (d) recirculating the liquid within each vat by means of a pump in a direction opposite to the movement of the fabric bags. In one embodiment, the dyed fabric is denim, and the liquid is a treatment liquid which is a member selected from the group consisting of dye solvent, aqueous reducing solution or aqueous bleach or dyes, chemicals or reagents that may assist in enabling optimization of the fabrics of this invention for utilization in subsequent processes or end use applications.

In summary, the process of this invention for removing dye from fabric carrying said dye comprises the steps of (a) moving a bag containing said fabric down a first longitudinal vat containing a liquid solvent for said dye at a level wherein longitudinal movement of liquid in the vat is blocked by the bag, whereby longitudinal movement of the bag and recirculation by means of a pump causes liquid solvent to flow through the bag in a direction counter to the movement of the bag; (b) moving the bag from the vat across a drainage platform to allow excess liquid solvent to flow from the bag; and (c) moving said bag containing said fabric down a second longitudinal vat containing liquid solvent for the dye at a level wherein longitudinal movement of the bag causes liquid solvent to flow through the bag in a direction counter to the movement of the bag. In one embodiment, the dyed fabric is denim, and the liquid is a solvent for indigo.

In another embodiment of the process of this invention for removing dye from fabric carrying

said dye comprises the steps of (a) moving a bag containing said fabric down a first longitudinal vat containing an aqueous solution containing a reducing and solublizing agent or said dye at a level wherein longitudinal movement of liquid in the vat is blocked by the bag, whereby longitudinal movement of the bag causes said aqueous solution to flow through the bag in a direction counter to the movement of the bag; (b) moving the bag from the vat across a drainage platform to allow excess aqueous solution to flow from the bag; and (c) moving said bag containing said fabric down a second longitudinal vat containing aqueous solution for the dye at a level wherein longitudinal movement of the bag and recirculation of the solution by means of a pump causes said aqueous solution to flow through the bag in a direction counter to the movement of the bag. In one embodiment, the dyed fabric is denim, and the aqueous solution contains a reducing and solublizing agent for indigo.

In another embodiment, the process of this invention for bleaching fabric carrying said dye comprises the steps of (a) moving a bag containing said fabric down a first longitudinal vat containing an aqueous solution containing a bleaching agent for said dye at a level wherein longitudinal movement of liquid in the vat is blocked by the bag, whereby longitudinal movement of the bag and recirculation of the solution by means of a pump causes said aqueous solution to flow through the bag in a direction counter to the movement of the bag; (b) moving the bag from the vat across a drainage platform to allow excess aqueous solution to flow from the bag; and (c) moving said bag containing said fabric down a second longitudinal vat containing aqueous solution for the dye at a level wherein longitudinal movement of the bag and recirculation of the solution by means of a pump causes said aqueous solution to flow through the bag in a direction counter to the movement of the bag. In one embodiment, the dyed fabric is denim, and the aqueous solution contains a bleaching agent for indigo. The bleaching agent can be hydrogen peroxide bleach containing a bleaching catalyst, optimally water-soluble quaternary amine catalyst.

In another embodiment, the fabric is bleached and/or decolorized (or partially decolorized) denim fabric and the trough solution contains dyes, chemical or reagents that may assist in enabling optimization of the fabrics of this invention for utilization in subsequent processes or end use applications.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic longitudinal cross-sectional view of an abbreviated trench processing system according to an aspect of this invention.

Fig. 2 is a top view of the trench processing system of Fig. 1 according to an aspect of this invention.

Fig. 3 is a cross-sectional view of a section of the trench processing system of Fig. 1 according to an aspect of this invention.

Fig. 4 is a cross-sectional view of the trench taken along the line 4-4 in Fig. 3 according to an aspect of this invention.

Fig. 5 is a cross-sectional view of the trench and fabric treatment bag taken along the line 5-5 in Fig. 3 according to an aspect of this invention.

Fig. 6 is a view of a typical scrap bag 16 according to an aspect of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The process of this invention is described hereinafter in terms of extracting dye from denim scrap and bleaching denim scrap because it is more demanding and requires description of more details than extracting and bleaching of dyed unfinished and finished cellulose fiber products such as clothing. Dye removal and bleaching of denim garments is desired to product products having a faded "stone-washed" appearance, for example. It will be readily understood to a person skilled in the art that the process of this invention can be applied to remove all or only a portion of the color in a dyed fabric or garment of cellulose or other material and all of these bleaching applications are intended to be included within the scope of this invention.

Fig. 1 is a schematic longitudinal cross-sectional view of an abbreviated trench processing system of this invention, and **Fig. 2** is a top view thereof. The trench system is a series of longitudinal elongated vats 2 optionally separated by raised drain platforms 4 with an untreated bag support platform 6 at the staging end and a processed bag support region of platform 8 at the receiving end. A drum pulley 12 driven by motor mounted on platform 8 reels in the endless loop of draw rope or cable 14. The draw rope 14 has rings 15 attached to it for shackling to bags filled with scrap 16 as shown in greater detail in **Fig. 6**. A matching drum pulley 18 supported on platform 6 reels and/or returns the draw rope to the staging platform for attachment of bags of scrap awaiting processing. The bags 16 are drawn through treatment liquid 10 in each vat.

Each vat has a liquid inlet pipe 17 and an outlet pipe 19, the outlet pipe from one vat being connected with a valve 21 to the inlet pipe of the adjacent vat for movement of liquid in a direction through the series of vats in a direction counter to the direction of movement of the bags 16. Additionally, each vat has a recirculation line 23 with a pump 25 which is used to recirculate liquor from the bag inlet end of the vat to the bag outlet end. The vats can have bottoms at the same elevation or they can progressively lower elevations in the direction of the liquid flow to use gravity to move the liquid between vats. Similarly, the bottom of each vat can be level or be sloped slightly upward in the direction of bag movement to facilitate liquid flow in the counter current direction. **Fig. 3** is a cross-sectional view of a section of the trench processing system of **Fig. 1**.

Each treatment vat 2 has a sloped inlet end 20 down which each bag is drawn into the treatment

liquid, a flat bottom 21, and a sloped outlet end 22 up which each bag is drawn to a draining platform 8.

Fig. 4 is a cross-sectional view of the trench taken along the line 4-4 in Fig. 3, and **Fig. 5** is a cross-sectional view of the trench and fabric treatment bag taken along the line 5-5 in Fig. 3. The bottom of the vat has a curved shape to which the bags conform. The treatment liquid level 26 is lower than the top 28 of the bag so the bag acts as a plug, forcing the liquid to flow through the contents of each bag as the bag is drawn through the vat.

Fig. 6 is a view of a typical bag 16. The bags have a conventional open mesh construction sufficiently close to retain the fabric scraps but not so close as to impede liquid flow. Each bag has a loop 34 which is attached by shackle 35 to ring 15 fixed to draw rope 14. Scrap typically has irregular shapes and sizes, and for uniform processing, cutting the fabric pieces, although not necessary, may be desirable. The scraps can be cut or chopped into these pieces using conventional fabric chopping equipment.

Because of the size and construction of the pieces of denim scrap, it is difficult to accomplish uniform processing in the bath processes for dye removal and bleaching. Denim is a twill fabric, hence is not a symmetrical weave. On the face side of the fabric, more warp yarn is exposed than fill yarn and on the other side, more fill yarn is exposed than warp yarn. In indigo dyed denim, the warp yarn is heavily dyed, and the fill yarn is undyed. Because of the asymmetry in construction and the different chemical history of the yarns, when denim scraps are wetted with solvent and agitated in a free state, they tend to curl and roll into spirals of fabric, sometimes tightly. A tightly wound spiral allows poor access in a circulating agitation bath since inner portions are shielded by the outer layers. As a further problem, agitation tends to unravel the scraps, producing useless balls and tangles of yarn, yarn pieces and fibers which foul the bath components.

This problem is solved by use of a trench treatment apparatus in the process of this invention because the liquid contact with the fabric and removal or bleaching of the dye molecules occurs in the slow moving liquid by a combination of liquid flow and diffusion which is not significantly impeded by the conformation of the fabric. Prolonged contact of the liquid with the fabric achieves the result. Furthermore, the fabric is not frayed by the slow movement of the liquid through the bag. Additionally, the packing configuration of the fabric pieces within the bag prevents fabric movement and no curling problems occur.

Referring to **Figs. 1** and **2**, after the denim scrap is placed in the mesh bag 16, the bag is placed on the untreated fabric platform 6 and shackled to the draw rope 14. The draw rope 14 pulls the filled bag

slowly into the first vat 2 where it is thoroughly wetted by the treatment liquid 10. The bag plugs the vat and extends above the top surface of the liquid 10. As the slow bag movement continues, the bag is very slowly drawn through the vat, liquid is pushed down the vat by the bag, raising the liquid level in front of the bag, the difference in liquid level causing the liquid to flow by gravity through the contents of the bag. Additionally, liquid is removed from the inlet end of the vat, passes through conduit 23, and is discharged into the outlet end of the vat by means of a pump 25. This increases the flow of liquid through the bag to a flow rate in excess of that produced by bag movement alone. As the bag movement continues, the bag is drawn up onto platform 8, above the liquid level, and the excess liquid drains from the bag. The bag is then drawn into the next vat of the series where the process is repeated until the bag is drawn from the final vat onto the treated fabric platform 8. The treatment liquid flows through the series of vats in a direction counter to the direction of movement of the fabric-filed bags, fresh liquid being introduced at the end of the last vat adjacent the treated fabric platform 8 to effect final treatment of the fabric with fresh liquid. The liquid is passed from vat to vat through the conduits 19 and 17 until its removal from the vat system adjacent the untreated fabric platform 6. In this manner, for dye removal by an aqueous reducing solution, the liquid removed from the system has the maximum concentration of dye, facilitating dye recovery, and the fabric from which the dye has been mostly removed has a final exposure to clean reducing solution. Similarly, for bleaching, the fabric at the end of the process is exposed to a maximum strength bleaching solution while the fabric first being introduced to the system has the maximum amount of dye and is exposed to a bleaching solution which can be almost exhausted. This is desirable to effect maximum bleaching efficiency with the chemical bleaching reagent.

It will be readily apparent to a person skilled in the art that any number of vats can be used, and special pretreatment vats and final, rinsing vats can be interposed with separate liquid supplies and waste lines, if the process requires these additional steps. The vats can be provided with conventional heating coils to maintain the vat solutions at a pre-selected elevated temperature, if desired.

Aqueous Dye Extraction Using a Reducing Agent

This process applies certain portions of the process of U.S. Patent No. 5,366,510, the entire contents of which are hereby incorporated by reference. After the denim scrap is placed in a bag 16 and

the bag are shackled to a ring 15, the bag is pulled into the adjacent vat into contact with an aqueous reducing solution. As the bag is pulled through a succession of vats and drain platforms and a stream of reducing agent solution slowly flows through the bag, the water-insoluble dye in the fabric is reduced by the reducing agent in the solution to a water-soluble form which then dissolves in the aqueous solvent and is removed from the fabric by diffusion and/or liquid movement.

The extraction solution is an aqueous solution of a reducing agent, preferably at an elevated temperature of about 80°C to 95°C. Depending upon the subsequent dye recovery process, advantageously a dye complexing agent such as polyvinyl pyrrolidone may be added to prevent redeposit of the degraded dye.

Suitable reducing agents which are useful for desizing starch type sizing and removing indigo and other vat dyes from denim scraps include alkali metal hydrosulfites, for example, sodium hydrosulfite; alkali metal sulfoxylate formaldehyde such as the sodium salt, thiourea dioxide, and the like.

Reducing agents which are primarily useful for removing the indigo and other vat dyes include alkali metal hydrogen sulfites, sulfides, thiosulfates, oxalates, hydrosulfites and hydrosulfides.

The most useful compounds for vat dyes are sodium hydrosulfite and sodium sulfoxylate formaldehyde and, for sulfur dyes, sodium sulfide.

Advantageously, sodium or zinc sulfoxylate formaldehyde is applied under either acid or basic conditions, and sodium hydrosulfite is used under basic conditions.

The amount of the reducing agent to be used is not critical, but stronger solutions are more efficient. A solution of from 0.5 to 20 grams per liter of thiourea dioxide or from 0.5 to 20 grams per liter of sodium hydrosulfite is suitable.

The reducing agent converts the indigo and other vat dyes in the fabric to their water soluble state, and the dye is carried into solution, removed from the fabric and passed to the drain from which it is captured for dye recovery.

Catalyzed Alkaline Hydrogen Peroxide Bleaching

After removal of the reducing solutions and rinsing with water to remove any remaining free-floating dye, the bags 16 can be placed into a second series of vats having the structure shown in **Figs. 1** and **2** where they are drawn through a catalyzed hydrogen peroxide bleaching solution. It will be readily

apparent to a person skilled in the art that the rinse treatment and the catalyzed hydrogen peroxide bleaching solutions can be provided in an extension of the dye removal vats or in a separate series having the same or a similar structure, and all configurations of vats and treatment solutions are intended to be included within the scope of this invention.

The hydrogen peroxide bleaching solution should have a concentration of hydrogen peroxide of from 0.2% to 3.0%. The concentration range is preferably from 0.25% to 1.0%. The solution pH is preferably within the range of from 10.5 to 11.2, and the process water temperature is preferably within the range of from 75° to 95°C. The addition of catalysts demands that the pH be maintained somewhat lower with catalyst than without catalyst, for example 10.7 with catalyst and 11.0 without. The use of higher temperatures accelerates the bleaching regardless of catalyst and improves the whiteness achieved.

This invention is based on the discovery that with appropriate catalysts, hydrogen peroxide can effectively decolorize dyes which have been selected to be oxidation resistant, even dyes which are routinely insolubilized with hydrogen peroxide without loss of color. And even more surprisingly, very satisfactory decolorizing is obtained without significant loss of fiber strength or fiber quality.

Suitable catalysts include transition metal ions, preferably cupric and stannic ions. Other transition metal ions such as chromium, cobalt and nickel also exhibit catalyst activity. The concentration of catalyst must be sufficient to catalyze the bleaching reaction but should be insufficient to cause spontaneous and rapid decomposition of the hydrogen peroxide. A catalyst concentration of from 0.1 to 2 ppm is usually operable and a concentration of from 0.3 to 0.7 ppm is preferred. Careful control of catalyst concentration is required.

Because these metal ion catalysts cause decomposition of the hydrogen peroxide at higher concentration, quantities of transitional metal ions normally present in conventional water can cause serious problems. Removal of these ions by ion exchange is usually necessary prior to the addition of the desired level of catalyst.

Chelates are coordination compounds having a multidentate ligands, that is, ligands which bond to a metal atom at more than one place in a process termed chelation. Any water-soluble chelating agent effective to complex and deactivate the catalytic activity of transition metal ions can be used. Suitable water-soluble chelating agents are EDTA (ethylenediaminetetraacetic acid) and NTA (nitrilotriacetic acid).

Water-soluble quaternary amines are preferred catalysts because they are not significantly

complexed and deactivated by conventional chelating agents. Suitable water-soluble quaternary amines include lower alkyl ammonium halides and their derivatives such as hydroxy and epoxy substituted (lower alkyl) trimethylammonium halides such as substituted propyltrimethylammonium chlorides. Preferred quaternary amines for use in the process of this invention are dihydroxypropyltrimethylammoniumchloride, chlorohydroxypropyltrimethylammoniumchloride and epoxypropyltrimethylammoniumchloride, for example.

These quaternary amine catalysts have been used to catalyze hydrogen peroxide bleaching of wood pulp. Wood pulp cellulose pigments are not selectively resistant to hydrogen peroxide, and the unique action of catalyzed hydrogen peroxide on vat dyes would not be predicted or suggested by their action in wood pulp.

The concentration of the quaternary amines in the hydrogen peroxide solution should be from 0.1 to 1.0% and is preferably from 0.1% to 0.5%.

Following the hydrogen peroxide bleaching, rinse water is passed through the scrap bed to remove residual bleach and catalyst. Following the washing step, treatment of the decolorized denim fabric with dyes, chemicals and reagents that may assist in enabling optimization of the fabrics of this invention for utilization in subsequent processes or end use applications can be added. Thus, the treatments may contain humectants, antibacterial agents, lubricants, dyes or tints, optical brighteners, hand modifiers, anti-static agents and the like.

After completion of the extraction, and if applied, the bleaching process, the bags are removed from the final solution and squeezed in a hydraulic press to reduce the rinse water content, the bag emptied, and the scrap fragments are treated to remove residual water or solution, that is, dried. The dried fragments are then passed through a conventional garnetting machine or similar device to separate the individual bleached cotton fibers. Subsequent processing will be determined by the desired use of the fibers. For production of yarn, the fibers are preferably blended with longer virgin fibers, carded and spun into yarn by conventional procedures. For medical cotton applications, the fibers are processed by the traditional manufacturing procedure developed for each use.

The process of this invention is further shown by the following specific but non-limiting examples.

EXAMPLE 1

Desizing and Dye Removal

For this process, a vinyl ester or epoxy FRP lined trench with a glass smooth gel coat backed by 2 inches of magnesite insulation and properly reinforced concrete is constructed. The trench is 4 feet wide and 9 feet deep (inside dimensions). At either end of the trench is a raised ground level platform 8 feet long. On the inlet end of the trench, the raised platform is used for loading incoming bags, and on the outlet end of the trench, the raised platform is used for removing outgoing bags. Immediately after the incoming bag platform the bottom of the trench slopes downward at a 45° angle to a flat bottom 10 feet deep and 6 feet long. This forms a deep vat which contains only water, not extraction liquor. Immediately before the outgoing bag platform is a similar deep section of trench, or vat, which is 8 feet long and 10 feet deep, and contains only water. These two vats which contain only water are used to effect water seals for the trench cover. Over the entire top of the trench is an insulated FRP lid with two inches of magnesite insulation that covers not only the trench, but also the pull rope and suspension pulleys for the pull rope. At each end of the trench, the pull rope and also the fabric bags drop below the level of the water in the vat. At each end of the FRP lid, the bottom edge extends downward below the surface of the water in the vat. Because the trench cover is sealed along the sides, the water seal on either end of the trench completely isolates the atmosphere inside of the cover and above the trench from surrounding air which contains oxygen. Because the sodium hydrosulphite solution within the trench reacts with atmospheric oxygen, this cover allows the air within to become almost completely depleted of oxygen content.

The water-containing vat on the bag discharge end also acts as a rinse chamber. Water is recirculated at 80 gallons per minute and 95°C through the fabric bag in the discharge water vat, and residual sodium hydrosulphite solution is removed. Water is fed to this water vat at the rate of 2000 gallons per hour and leaves as effluent at the same rate. Immediately before this rinse vat, there are two other rinse vats with 8 ft. flat bottoms and separated from preceding and following vats by 4 foot long, 4-1/2 foot high flat topped platforms. The fronts and backs of each of these raised platforms slope seamlessly downward at 45° angles to the bottoms of the longitudinal vats. The makeup water is fed to the last vat in the direction of bag movement and removed from the first vat. The used rinse water contains caustic, sodium hydrosulfite, and some dye and therefore advantageously is piped directly to the last dye extraction vat as makeup water for the extraction liquor.

The extraction section of the trench consists of four vats, 9 feet deep with 8 feet flat bottoms. These vats are separated by raised platforms, 4-1/2 feet high with four foot flat tops. The fronts and backs of each of these raised platforms slope seamlessly downward at 45° angles to the flat bottoms of the vats. In this manner, the trench is divided into longitudinal vats through which bags of fabric are pulled. CPVC or other corrosion resistant piping is attached to slots at each end of the bottom of each longitudinal vat in such a manner that liquid may pass from vat to vat bypassing each raised platform. Additionally, the drain slot at the bag inlet end of each vat is connected to a corrosion resistant pump which discharges through piping to a liquor inlet slot at the bag outlet end. The liquor inlet slot extends across the full width of the trench, and in operation, liquor is forced upward through each bag as it passes over the slot. The pump suction slot extends across the full width of the trench, and in operation, pulls liquid downward through each bag as it passes over the slot. In this manner, liquor may be recirculated through each vat in a direction opposite to the direction of movement of the bags.

Heavy polyester mesh bags with approximately 1/4 inch openings are fabricated having dimensions such that pulling a full bag through the trench forms a cubic fabric plug of approximately 4 ft. height, width, and length. The bags are loaded with approximately 720 pounds of denim cutting room scrap dyed with both indigo dye and black sulfur dye. Before loading into the bags, the cutting room scrap is cut into pieces with an average maximum dimension of 2 inches.

Bags are attached by rope loops and shackles to heavy metal stainless steel rings located down the draw rope at 8 foot intervals. The bag interval is therefore one bag every 8 feet. The draw rope is held suspended on pulleys at an elevation slightly below the top of the trench. The draw rope consists of a continuous loop which is pulled by a sheave at a rate of 0.37 ft. per minute.

Each of the longitudinal vats is recirculated by means of a pump at a rate of 80 gallons per minute. This gives an average 5 gallons per minute per square ft. face velocity of liquor passing through the bag. Liquor is passed through the entire extraction trench at a rate of 2000 gallons per hour. This liquor is pumped into the vat at the end of the trench from which the bags go into the rinse section. Discharge liquor containing a high concentration of dye is pumped out of the vat at 2000 gallons per hour at the end where the bags are fed into the trench process. This high concentration of dye in the liquor effluent facilitates easy subsequent recovery of the dye and a minimal use of water in the process. The incoming extraction liquor is made up of 2000 gallons per hour at 95° C water, 295 pounds of 38° Baume caustic soda solution, 50 pounds of 95% sodium hydrosulfite, and 23 pounds of Amwet PTH wetter

solution (made by American Emulsions) and 28 pounds of 40% polyvinylpyrrolidone. As the liquor passes into each subsequent longitudinal vat, 20 pounds of sodium sulfite and 24 pounds of 38° Baume caustic soda are added. This replaces that sodium sulfite which naturally degrades with time and adjusts the pH because of the added reagent.

As the bags of fabric leave the extraction trench, they are uniformly depleted of indigo and black sulfur dyes, and the fabric is a very light blue. At this point, it is ready for bleaching with either a peroxide or a sodium hypochlorite bleach process.

EXAMPLE 2

Catalyzed Hydrogen Peroxide Bleaching

Bags containing very light blue denim scrap that has been desized and from which the dye has been extracted are moved from the extraction and desizing device to the end of a bleaching trench. For this process, a vinyl ester or epoxy FRP lined trench with a glass smooth gel coat backed by 2 inches of magnesite insulation and properly reinforced concrete is constructed. The trench is 4 feet wide and 9 feet deep (inside dimensions). At either end of the trench is a raised ground level platform 8 feet long. On the inlet end of the trench, the raised platform is used for loading incoming bags, and on the outlet end of the trench, the raised platform is used for removing outgoing bags. The entire length of trench is covered with a FRP lid backed with two inches of urethane foam insulation.

Immediately before the outgoing bag platform the trench slopes down to a flat bottomed vat which is 8 feet long, 9 feet deep, and contains wash water. Water is recirculated at 80 gallons per minute and 95°C through the fabric bag in the discharge water vat, and residual bleach bath liquor is removed. Water is fed to this water vat at the rate of 2000 gallons per hour and leaves as effluent at the same rate. Immediately before this rinse vat, there are two other rinse vats of the same dimensions. All of the rinse vats are separated by raised platforms 4-1/2 ft. above the bottom of the trench and 4 feet long. The front and back of each of these raised platforms slope seamlessly downward at 45° angles. The resulting troughs, or vats, between raised platforms are 8 feet long. The makeup water is fed to the last vat in the direction of bag movement and removed from the first vat. The used rinse water contains caustic, peroxide, sequesterant, and some bleach bath chemicals and therefore advantageously is piped directly to

the bleach vats as makeup water. To the first rinse vat, the one nearest the bleach vat, is added 17 pounds per hour of 60% acetic acid, 50 pounds of Delimol NSR (wetting and scouring agent manufactured by BASF), and 21 pounds of Delimol 9208 (dye dispersant and water sequesterant manufactured by BASF). Each rinse vat has its own recirculation pump. The recirculation pump passes the rinse water through the bags at 80 gallons per minute and washes bleach bath liquor from the bags. Because each rinse vat has its own recirculation pump, the bleach bath liquor concentration is highest in the first rinse vat and lowest in the last rinse vat. The rinse water, moving counter to the direction of bag movement passes from the first rinse vat to the last bleach vat. Acetic acid is added to the makeup water in the rinse bath to neutralize the alkalinity coming into the rinse vats from the bleach vats.

Before the rinse vats in the direction opposite to bag movement, the trench consists of three bleaching vats. The bleaching vats have flat bottoms which are 8 feet long and are separated by raised platforms 4-1/2 feet across the top with both a front surface and a back surface which slope seamlessly downward at 45 degrees to the flat bottoms of the vats. In this manner, the trench is divided into longitudinal vats through which bags of fabric are pulled. CPVC or other corrosion resistant piping is attached to slots at each end of the bottom of each longitudinal vat in such a manner that liquid may pass from vat to vat bypassing each raised platform. Additionally, the drain slot at the bag inlet end of each vat is connected to a corrosion resistant pump which discharges through piping to a liquor inlet slot at the bag outlet end. The liquid inlet slot extends across the full width of the trench, and in operation, liquor is forced upward through each bag as it passes over the slot. The drain slot extends across the full width of the trench, and in operation, pulls liquid downward through each bag as it passes over the slot. In this manner, liquor may be recirculated through each vat in a direction opposite to the direction of movement of the bags.

Heavy polyester mesh bags with approximately 1/4 inch openings are fabricated having dimensions such that pulling a full bag through the trench forms a cubic fabric plug of approximately 4 ft. on each side. The bags are loaded with approximately 720 pounds of denim cutting room scrap originally dyed with both indigo dye and black sulfur dye, but from which most of the dye has been extracted utilizing a reducing agent. This cutting room scrap consists of pieces with an average maximum dimension of 2 inches.

Bags are attached by rope loops and shackles to heavy metal stainless steel rings located down the draw rope at 8 foot intervals. The bag interval is, therefore, one bag every 8 feet. The draw rope is held

suspended on pulleys at an elevation slightly below the top of the trench. The draw rope consists of a continuous loop which is pulled by a sheave at a rate of 0.37 ft. per minute.

Each of the longitudinal vats is recirculated by means of a pump at a rate of 80 gallons per minute. This gives an average 5 gallons per minute per square ft. face velocity of liquor passing through the bag. Makeup liquor is fed to the bleaching vats from the rinse vats at a rate of 2000 gallons per hour. This liquor is pumped into the bleach vat immediately upstream (i.e. counter to bag movement) of the first rinse vat. To the makeup liquor coming from the rinse section is fed 168 lbs./hr. of 35% hydrogen peroxide, 134 lbs./hr. of 38° Baume caustic soda, and 84 pounds of 20% dihydroxyporpyltrimethylammonium chloride solution.

The bleach bath liquor is level controlled to a pump which removes it from the first bleach vat. This liquor is then treated in such a way as to render it acceptable for disposal and is discharged into the plant waste water stream.

The fabric scrap has been bleached to a uniform CIE brightness of 85 and is ready for dewatering and drying.

EXAMPLE 3

Sodium Hypochlorite Bleaching

Bags containing very light blue denim scrap that has been desized and from which the dye has been extracted are moved from the extraction and desizing device to the end of a bleaching trench. For this process, a vinyl ester or epoxy FRP lined trench with a glass smooth gel coat backed by 2 inches of magnesite insulation and properly reinforced concrete is constructed. The trench is 4 ft. wide and 9 ft. deep (inside dimensions). At either end of the trench is a raised ground level platform 8 ft. long. On the inlet end of the trench, the raised platform is used for loading incoming bags, and on the outlet end of the trench, the raised platform is used for removing outgoing bags. The entire length of trench is covered with a FRP lid backed with 2 inches of urethane foam insulation.

Immediately before the outgoing bag platform the trench slopes down to a flat bottomed vat which is 8 feet long, 9 ft. deep, and contains wash water. Water is recirculated at 80 gallons per minute and 95°C through the fabric bag in the discharge water vat, and residual bleach bath liquor is removed.

Water is fed to this water vat at the rate of 2000 gallons per hour and leaves as effluent at the same rate. Immediately before this rinse vat, there are two other rinse vats of the same dimensions. All of the rinse vats are separated by raised platforms 4-1/2 ft. above the bottom of the trench. The front and back of each of these raised platforms slope seamlessly downward at 45° angles to the flat bottoms of the adjacent vats. The makeup water is fed to the last vat in the direction of bag movement and removed from the first vat. The used rinse water is discharged into the plant waste water effluent stream for proper treatment and disposal. To the first rinse vat, the one nearest the bleach vat, is added 10 pounds per hour of 60% acetic acid and 25 pounds of sodium thiosulfate. Each rinse vat has its own recirculation pump. The recirculation pump passes the rinse water through the bags at 80 gallons per minute, washes bleach bath liquor from the bags, and neutralizes any remaining sodium hypochlorite bleach. Acetic acid is added to the makeup water in the rinse bath to neutralize the alkalinity coming into the rinse vats from the bleach vats.

Before the rinse vats in the direction opposite to bag movement, the trench consists of three bleaching vats. Each bleaching vat has a flat bottom 8 feet long, and at both ends slope upward at 45° angles to form raised platforms 4 ft. in length across the top and approximately 4-1/2 ft. above the bottom of the trench. In this manner, the trench is divided into longitudinal vats through which bags of fabric are pulled. CPVC or other corrosion resistant piping is attached to slots at each end of the bottom of each longitudinal vat in such a manner that liquid may pass from vat to vat bypassing each raised platform. Additionally, the drain slot at the bag inlet end of each vat is connected to a corrosion resistant pump that discharges through piping to a liquor inlet slot at the bag outlet end. The liquor inlet slot extends across the full width of the trench, and in operation, liquor is forced upward through each bag as it passes over the slot. The drain slot extends across the full width of the trench, and in operation, pulls liquid downward through each bag as it passes over the slot. In this manner, liquor may be recirculated through each vat in a direction opposite to the direction of movement of the bags.

Heavy polyester mesh bags with approximately 1/4 inch openings are fabricated having dimensions such that pulling a full bag through the trench forms a cubic fabric plug of approximately 4 ft. on each side. The bags are loaded with approximately 720 pounds of denim cutting room scrap originally dyed with both indigo dye and black sulfur dye, but from which most of the dye has been extracted utilizing a reducing agent. This cutting room scrap consists of pieces with an average maximum dimension of 2 inches.

Bags are attached by rope loops and shackles to heavy metal stainless steel rings located down the draw rope at 8 foot intervals. The bag interval is, therefore, one bag every 8 feet. The draw rope is held suspended on pulleys at an elevation slightly below the top of the trench. The draw rope consists of a continuous loop which is pulled by a sheave at a rate of 0.37 ft. per minute.

Each of the longitudinal vats is recirculated by means of a pump at a rate of 80 gallons per minute. This gives an average 5 gallons per minute per square ft. face velocity of liquor passing through the bag. Makeup water is fed to the bleaching vats from the rinse vats at a rate of 2000 gallons per hour. This water is pumped into the bleach vat immediately upstream (i.e. counter to bag movement) of the first rinse vat. To the makeup water are added 270 lbs./hr. of 10% sodium hypochlorite bleach and 50% caustic soda solution at the rate required to raise the liquor pH to 10.5.

The bleach bath liquor is level controlled to a pump that removes it from the bleach vat which bags first enter. This liquor is then treated in such a way as to render it acceptable for disposal and is discharged into the plant waste water stream.

At this point, the fabric scrap has been bleached to a uniform CIE brightness of 85 and is ready for dewatering and drying.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.